BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1504—1509 (1969)

Moderator Effects on the Reactions of ^{82}Br Activated by the Isomeric Transition with Gaseous Methyl Bromide

Jiro Okamoto and Enzo Tachikawa

Division of Chemistry, Japan Atomic Energy Research Institute, Tokai-Mura, Ibaraki

(Received October 22, 1968)

^{82}Br obtained *via* the (I. T.) process has been reacted with methyl bromide. In the gaseous phase, only $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ are observed as major products, whereas in the solid phase other products, such as $CH^{82}BrBr_2$ and $C_2H_5{}^{82}Br$, have also been observed. Moderator experiments using He or Xe indicate that the formations of both $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ involve the reactions of the energetic ^{82}Br atom. This is in great contrast to the early observations of the Br_2-CH_4 system, where the ionic as well as the energetic reactions of ^{82}Br play a role in the formation of the C-^{82}Br bond. Comparisons of these results with those found in the reactions of the ^{80}Br obtained *via* the (n, γ) process suggest that the Br atom obtained *via* the (n, γ) process is more electronically excited than that from the (I. T.) process. The kinetic analysis of the present results gives the following relative α-values: α_{He}, 1.0; α_{Xe}, 8.8; α_{CH_3Br}, 10.3. It is suggested that, during the cooling-down process of ^{82}Br, a high inelasticity is involved in the collision of ^{82}Br, even with monatomic molecules.

Investigations of the recoil halogen atom reaction have included studies designed to find out more about both the primary physical state and the chemical process, and the mechanisms of chemical stabilization following these processes.$^{1-5)}$

Predominant among the subjects of interest is the relative importance of the kinetic energy and of the charge in determining the chemical reaction of the recoil atom. Definitive evidence$^{6)}$ exists that the energetic reaction and also the ionic reaction sometimes play important roles in a gaseous-phase reaction of the halogen atom activated by the (n, γ) process, only part of which atom is positively charged.$^{7,8)}$

A high charge on the Br atom is developed as a consequence of the Auger process following the isomeric transition. It is postulated that this highly positive charge is partially neutralized by electron transfer from the remainder of the molecule, thus causing a repulsive force between the charged bromine atom and the remainder of the molecule.$^{9)}$ The studies using a charge spectrometer indicate that free bromine atoms resulting from a molecular explosion show a charge distribution ranging up to $+14$.$^{10)}$ The electron affinity of such a highly charged bromine is so high that its subsequent reaction is an electron pick-up from its surroundings.$^{11)}$ Therefore, the important consideration is whether or not the Br^{+1} is reduced before reacting.

In the ^{82}Br-CH_4 system,$^{3)}$ $CH_3{}^{82}Br$ is formed by the hydrogen substitution reaction of the energetic ^{82}Br atom, while $CH_2{}^{82}BrBr$ is formed *via* the ion-molecule reaction of $^{82}Br^{+1}$. The ionization potential of methyl bromide is 10.6 eV,$^{12)}$ which is lower than that of bromine by 1.2 eV. This suggests the ionic reaction of ^{82}Br is less significant in an atmosphere of methyl bromide.

The present paper is concerned with a detailed study of the reaction of the ^{82}Br obtained *via* the (I. T.) process with methyl bromide. Two reactions which are conceivable for the energetic ^{82}Br atom can be written for this compound as Eqs. (1) and (2):

$$^{82}Br + CH_3Br \rightarrow CH_3{}^{82}Br + Br \quad (1)$$

$$^{82}Br + CH_3Br \rightarrow CH_2{}^{82}BrBr + H \quad (2)$$

The isolation of these hot reaction products in other reactions, such as ionic or thermal, is possible

---

1) J. E. Willard, "Chemical Effects of Nuclear Transformations," Vol. I, IAEA, Vienna (1965), p. 221.

2) L. D. Spicer and A. A. Gordus, *ibid.*, p. 185.

3) E. Tachikawa and J. Okamoto, submitted to *J. Phys. Chem.*

4) R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 97 (1965).

5) F. Schmidt-Bleek and F. S. Rowland, *Angew. Chem. Internat. Edit.*, **3**, 769 (1964).

6) E. P. Rack and A. A. Gordus, *J. Chem. Phys.*, **34**, 1855 (1961).

7) E. P. Rack and A. A. Gordus, *ibid.*, **36**, 282 (1962).

8) S. Wexler and H. Davis, *ibid.*, **20**, 1688 (1952).

9) T. A. Carlson and M. R. White, "Chemical Effects of Nuclear Transformations," Vol. I, IAEA, Vienna (1965), p. 23.

10) S. Wexler, *ibid.*, Vol. 1 (1961), p. 115.

11) A. R. Kazanjian and W. F. Libby, *J. Chem. Phys.*, **42**, 2779 (1965).

12) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York (1957) Appendix.

through moderator and scavenger methods. The abstraction of the hydrogen or bromine atom in methyl bromide must also be considered as a possible reaction. However, experimental means are not available for tracing these reactions.

A series of experiments on the rigid phase,[1,13] indicative of a high yield of organically-bound ^{82}Br, have promoted a search for such a rigid phase in the present system.

Experimental

Materials. The bromine was obtained from the Kanto Chemical Company. Methyl bromide form the Tokyo Kasei Co. was purified several times by vacuum distillation techniques: gas chromatography showed no impurity greater than 0.01%. Helium and Xenon supplied by the Nihon Sanso Co. and the Takachiho Chemical Co., were used directly without additional purification (the listed purities are 99.999 and 99.995% respectively).

Sample Preparation and Irradiation. The preparation of samples followed the routine procedures used in our previous work for gas-phase bromine hot-atom chemistry.[3] A quartz capillary containing Br_2 was gas irradiated in a pneumatic tube of a Cp-5-type reactor in JAERI for 5 min. Then it was quickly inserted into a Pyrex ampoule filled with the required gases. About 10—20% of the ^{82m}Br formed during the irradiation decayed in the Pyrex ampoule, the ^{82}Br freshly formed was made to react with methyl bromide.

Radio-gas Chromatography. The organic products were separated using a dioctyl sebacate column (15% in weight) 3m long and 6mm in inside diameter. The temperature of the operation was 95°C. A short glass column containing pottasium ferrocyanide was placed before the separation column in order to isolate any inorganic bromides, such as $H^{82}Br$ or $Br^{82}Br$, formed in the reaction system. Otherwise, a gradual elution of these from the column would interfere with a precise radioactive assay of the organic bromide. Elution gas was introduced into a G-M counter in conjunction with a scaler and printer for radioactivity measurements of each product. For the determination of the absolute yields of the individual products, the total bromine activity was measured with a gamma-ray scintillation counter (a 2″+2″ well-type NaI(Tl) scintillator at 20 cm), after a complete decaying-out of the ^{80}Br (about 48 hr after irradiation).

Correction and Experimental Errors. All of the data obtained have been corrected for decays of ^{82m}Br and ^{82}Br according to the reported half-lives of 6.1 min[14,15] and 35.4hr respectively. A consideration of the kinetic energy of the ^{82}Br atom achieved by the Auger process following the isomeric transition of ^{82m}Br shows that the recoil loss of ^{82m}Br into the wall can be neglected in the pressure range studied.[11]

In most cases, the activity in $CH_3{}^{82}Br$ or $CH_2{}^{82}BrBr$ was large enough to reduce the standard deviation of counting to a small percentage. The relative short half-life of ^{82m}Br, is however, responsible for the most serious error in the absolute yields. A ninety-one percent radioactive neutron capture by ^{81}Br results in ^{82m}Br. At the end of a 5-min irradiation, 71% of the ^{82m}Br produced is still alive.

However, this is reduced to 10—20% upon the mixing of ^{82m}Br with methyl bromide, as the transit from the reactor to the laboratory and the following sample processing usually take 10—15 min. The yields of individual products constitute only a small percentage of the total ^{82m}Br produced originally. Therefore, the accuracy of these experiments is usually limited to 5%, except in a few cases in which the counting error was greater than normal.

Results

Samples were dipped into liquid nitrogen for varying periods of time (Δt) after the mixing of ^{82m}Br with methyl bromide. Such a method makes it possible to follow the reactions occurring in both the gaseous and solid phases in a series of experiments. In Table 1 the yields of the products are listed in connection with the Δt. The decrease in

TABLE 1. PERCENT YIELDS OF PRODUCTS AS A FUNCTION OF Δt

Filling pressure		Δt	Products (%)			
Br_2 (cmHg)	CH_3Br (cmHg)		$CH_3{}^{82}Br$	$CH_2{}^{82}BrBr$	$CH^{82}BrBr_2$	$CH_3CH_2{}^{82}Br$
5.0	45.0	∞	4.69±0.20	1.25±0.06	0.24±0.02	—
5.0	45.0	40 min	4.40±0.20	1.80±0.09	0.35±0.02	—
5.0	45.0	25 min	3.41±0.15	1.95±0.10	0.33±0.03	—
5.0	45.0	15 min	5.12±0.25	3.15±0.15	0.50±0.03	0.10±0.02
5.0	45.0	10 min	6.89±0.30	4.54±0.20	0.60±0.04	0.17±0.03
5.0	45.9	7 min	8.27±0.40	6.30±0.30	0.97±0.05	0.37±0.03
5.0	45.9	2 min	14.14±0.70	9.19±0.40	—*	0.31±0.03
5.0	45.9	1 min	15.07±0.70	10.79±0.50	1.78±0.06	0.38±0.02
5.0	45.9	30 sec	16.93±0.80**	10.45±0.50	—*	—

* Measurement was failed by a printing trouble.

** ($CH_3{}^{82}Br+CH_3CH_2{}^{82}Br$) is listed.

---

[13] J. A. Merrigan, W. K. Ellgren, Jr., and E. P. Rack, *J. Chem. Phys.*, **44**, 174 (1966).

[14] J. E. Emery, *J. Inorg. Nucl. Chem.*, **27**, 903 (1965).

[15] O. U. Anders, *Phys. Rev.*, **138**, B1 (1965).

the yields with the time is just the opposite of the increase found in the Br_2-CH_4 system.³⁾ This observation implies that a homogeneous mixing of the Br_2 and CH_3Br is also attained on the solidification of the mixture and the chemical reaction of the ^{82}Br from (I. T.) with methyl bromide proceeds. By contrast, in the Br_2-CH_4 system the solidification of a mixture has a clumping effect on bromine, so that bromine atoms undergoing a nuclear transformation are surrounded by an envelope of molecular bromine. Further chemical reaction of ^{82}Br with methane should thus be prevented. These two kinds of observations have also been made in solid-liquid intersystems.⁷⁾

In the following gaseous experiments, the quantitative measurements of $CH^{82}BrBr_2$ and $C_2H_5{}^{82}Br$ were not successful, simply because of their small yields (less than 0.2%). Thus, we weighted the quantitative measurements only for the products, $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$.

Table 2. Percent yields of $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ at varying pressure of methyl bromide

Filling pressure		Products (%)	
Br_2 (cmHg)	CH_3Br (cmHg)	$CH_3{}^{82}Br$	$CH_2{}^{82}BrBr$
5.0	1.8	0.32±0.02	0.21±0.02
5.0	5.7	0.85±0.04	0.43±0.03
5.0	9.5	1.32±0.07	0.59±0.04
5.0	14.2	2.01±0.10	0.65±0.05
5.0	20.1	1.87±0.10	0.79±0.05
5.0	30.6	3.78±0.19	0.58±0.03
5.0	40.6	>2.06±0.10*	>0.61±0.03*
5.0	30.9	3.08±0.15	1.23±0.06
5.0	45.9	4.68±0.24	1.25±0.06
5.0	76.6	5.89±0.29	2.29±0.12

* Part of the sample is lost during the sample processing.

Table 2 shows the dependences of the two major products on the pressure of methyl bromide, in the constant presence of 5 cmHg Br_2 as a scavenger. The observed increases in yields with the total pressure are considered to originate as follows: 1) with pressure, recoil loss into the wall is reduced; concomitantly, the amount of ^{82}Br reacted in the gaseous phase increases; 2) both products are formed *via* a ion-molecule reaction of $^{82}Br^{+1}$; 3) the primary products, $(CH_3{}^{82}Br)^*$ and $(CH_2{}^{82}BrBr)^*$, are highly excited, and their unimolecular decomposition reactions compete greatly with collisional deactivations as the pressure increases. The recoil energy of the ^{82}Br from (I. T.) is most in the range of 100 eV,⁹⁾ and the recoil loss of ^{82}Br into the wall is well below the experimental uncertainty in the pressure range studied. Thus, the first possibility above may be excluded.

One method to differentiate one possibility from the others is through the sensitivities of the reacting species to the addition of moderators. The dependency of the yields upon the mole fraction of helium or xenon added as a inert moderator has been measured. The results are shown in Figs. 1 and 2, where the yields are plotted as a function of the mole fraction of the moderator. In all the samples 5 cmHg of Br_2 is present as a scavenger, while the total pressure was always kept at 51±1 cmHg.

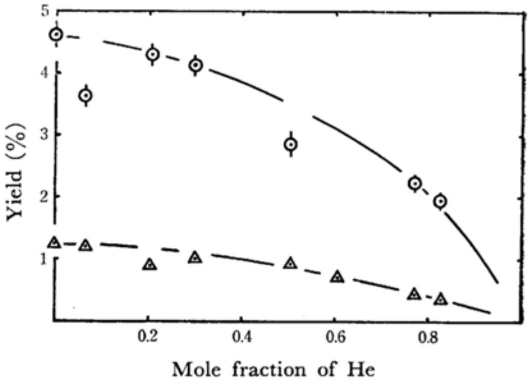

Fig. 1. Dependencies of $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ on the m.f. of He as a moderator.
(total pressure: 51±1 cmHg)
⊙: $CH_3{}^{82}Br$ △: $CH_2{}^{82}BrBr$

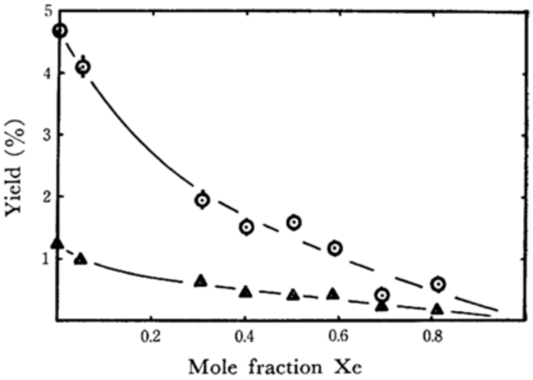

Fig. 2. Dependencies of $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ on the m.f. of as a moderator.
(total pressure: 51±1 cmHg)
⊙: $CH_3{}^{82}Br$ △: $CH_2{}^{82}BrBr$

Discussion

The most striking feature of the formation of the main products, $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$, is their great sensitivity to the presence of the moderating gas. Behavior of this kind can be understood if they formed by the energetic reaction of the ^{82}Br atom, not by the thermal ionic ^{82}Br atom. The ease with which $^{82}Br^{+1}$ is neutralized to the ^{82}Br neutral atom is dependent upon the ionization potential of the colliding partner in the system. As the ionization potential of methyl bromide is 10.6 eV, lower than that of Br (11.84 eV), the neutralization of Br^{+1} in collision with methyl bromide is energetically very much favored. Allowing this, the subsequent reaction of $^{82}Br^{+1}$ in collision with methyl bromide will be a discharging.

Although other minor products, such as $CH^{82}BrBr_2$ and $C_2H_5{}^{82}Br$, could not be measured quantitatively, their yields are so small that they can explain only a small percentage of the total organic products at most. Within this limitation, the ^{82}Br from (I. T.) reacts with methyl bromide as a hot ^{82}Br, and $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ are formed through the *^{82}Br for Br* and *^{82}Br for H* reactions, as has been shown in Eqs. (1) and (2).

On the other hand, previous experiments have shown that the ^{82}Br from (I. T.), in an atmosphere of methane and in the presence of Br_2 as a scavenger, reacts with methane *via* ionic as well as energetic reactions.[3,16] However, the ionization potential of methane is higher than that of Br, and the charge transfer reaction between Br^{+1} and CH_4 is calculated to be endothermic by *ca.* 1.3 eV. The different reactivities in ^{82}Br in these systems thus, leads to the following qualitative interpretations for the reaction mechanisms of ^{82}Br from (I. T.): if the ionization potential of a reactant is lower than that of Br, ^{82}Br can well be neutralized to a neutral ^{82}Br atom and reacts *via* energetic reactions. However, in a system in which the reactant has a higher ionization potential than does Br, part of the ^{82}Br may react *via* ion-molecule reactions prior to the complete neutralization. The higher the endothermicity of the neutralization reaction, $Br^{+1}+M \rightarrow Br+M^{+1}$, the more significant become the ionic reactions.

Rack and Gordus[17] have reported that the reactions of a ^{80}Br atom activated by $^{79}Br(n, \gamma)$-^{80}Br with CH_4 require only a kinetically-excited ^{80}Br atom in spite of the fact that originally at least 18% of the ^{80}Br atoms were positively charged.[18] It is, however, very likely that charge transfer will occur in a collision of Br^{+1} with CH_4 if the ion is electronically excited[18,19] in a state sufficiently high to overcome the endothermicity of the charge transfer reaction. If this is the case, the difference in the reaction mechanisms of Br atoms from different nuclear reactions can be connected with the electronic state of atoms when they are born. Thus, it may be suggested that the recoil atom resulting from the (n, γ) process is more likely to be electronically-excited than that resulting from the (I. T.) process. This discussion will have one feature in common with the results of Rack and Gordus[6,7] on the reaction of ^{128}I from $^{127}I(n, \gamma)^{128}I$ with methane, where reactions required electronically-excited ions as well as atom or ions of kinetic energy. However, the final answer to this problem must await more information concerning the physical state of the recoil atom obtained from other types of experiments.

Unimolecular Decompositions. The above discussions assist the interpretation of the results shown in Table 2 in terms of the competition between the decomposition and the collisional stabilization of the excited $(CH_3{}^{82}Br)^*$ and $(CH_2{}^{82}BrBr)^*$. These are formed by substitution reactions of hot ^{82}Br with sufficient internal excitation energy to cause secondary decomposition. Thus, the fate of the excited molecules is either stabilization by collisional deactivation with their surrounding molecules or unimolecular decomposition. The increase in the pressure serves to stabilize with an increase in the collision frequency.

Some information on the decomposition reactions of these excited molecules has been provided by studies of recoil tritium reaction. Rowland and his collaborators[20-23] have extensively studied the unimolecular decomposition reaction of internally-excited molecules formed by the substitution reaction of the recoil tritium atom. It is reasonable to assume that the chemical reaction range of the substitution reaction of the recoil T or ^{82}Br atom is not different enough to alter the decomposition paths of the resulting excited molecule.[24] Thus, very possibly the subsequent reaction of $(CH_3{}^{82}Br)^*$ or $(CH_2{}^{82}BrBr)^*$ will be:

$$(CH_3{}^{82}Br)^* \rightarrow CH_3 + {}^{82}Br$$

$$(CH_2{}^{82}BrBr)^* \rightarrow CHBr + H^{82}Br$$

$$\text{or} \quad CH^{82}Br + HBr$$

Factors Affecting the Yields. The higher yield in the solid phase is due simply to the combination of the ^{82}Br atom with the radicals formed by the radiation chemistry in the system.[11,25,26]

The present experiments were conducted in

---

16) E. P. Rack, Progress Report, Univ. of Nebraska, 1965.

17) E. P. Rack and A. A. Gordus, *J. Phys. Chem.*, **65**, 944 (1961).

18) C. E. Moore, "Atomic Energy Level," Natl. Bur. Standards, NO 67 (1952), p. 161.

19) J. D. Morrison, H. Hurzeler and M. G. Ingram, *J. Chem. Phys.*, **33**, 821 (1960).

20) E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 879 (1963).

21) Y. N. Tang and F. S. Rowland, *ibid.*, **90**, 574 (1968).

22) Y. N. Tang and F. S. Rowland, *ibid.*, **90**, 570 (1968).

23) Y. N. Tang and E. K. C. Lee and F. S. Rowland, *ibid.*, **86**, 1280 (1964).

24) Y. N. Tang and F. S. Rowland, *J. Phys. Chem.*, **71**, 4576 (1967).

25) P. R. Geissler and J. E. Willard, *ibid.*, **67**, 1675 (1963).

26) P. R. Geissler and J. E. Willard, *J. Am. Chem. Soc.*, **84**, 4627 (1962).

the absence of γ-radiation from a nuclear reactor. Alternatively, electrons emitted by the ^{82}Br atom as a result of internal conversion and Auger transitions produce a high localized concentration of radicals so close to the atom that their reactions with the atom are not precluded by the Br_2 scavenger, whereas in the gas phase these radicals can easily be scavenged.

One of the most important conclusions to be drawn from the present experiments is that the total organic yield *via* a hot reaction is less than 10%. This is parallel to the observations on other recoil halogen atom reactions[27,28] and is consistent with the proposal of Rowland *et al.*[28] They ascribed the fact that these yields are lower than those in the recoil tritium reaction to the ease with which a recoil atom can change direction in response to a newly-available chemical potential. The halogen atom, heavier than the tritium atom, may very well be hindered by such bond formation; a substantially lower yield than in the corresponding tritum system will result. Although corrections for the secondary decompositions of excited molecules sholud be made in quantitative discussions, such corrections are unlikely to alter the qualitative conclusion.

Kinetic Theory. One of the assumptions involved in the Estrup-Wolfgang kinetic theory[29,30] is that the initial energy of recoil atom is sufficiently high for the atom to have made number of collisions in order to attain the statistical distribution of energies for the atoms in the reaction range. Qualitatively this assumption is plausible. In the isomeric transition of ^{80m}Br in the molecular bromine, the resulting ^{80}Br atoms show a charge spectrum ranging up to +11, with a maximum between +4 and +5.[10] The average kinetic energy of the Br arom achieved from the molecular explosion of Br_2 can thus be estimated[9] to be over 100 eV. Since precise information on the kinetic energy spectrum of ^{82}Br is not available, this could serve as a reasonable approximation.

The developed equation is given in:

$$\frac{-1}{\ln(1-P)} = \frac{\alpha_{\mathrm{react}}}{I} - \frac{\alpha_{\mathrm{mod}}}{I}\left(\frac{1-f}{f}\right),$$

where P is the total probability (organic yield) of a hot atom combining in any hot product and where I is the corresponding total reactivity integral. α_{react} and α_{mod} are the average logarithmic energy loss per collision for reactant and moderator respectively. f, the collision fraction, is computed using:

$$f = \frac{X_{\mathrm{CH_4}} S_{\mathrm{CH_4}}}{\sum X_i S_i}.$$

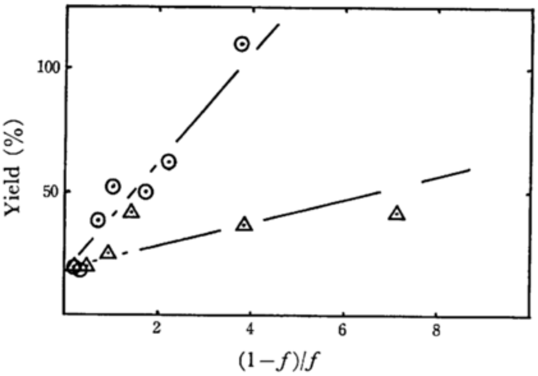

Fig. 3. Kinetic plotts of the total yields of products in moderated reactions of ^{82}Br with methyl bromide.

△: He moderator ⊙: Xe moderator

Table 3. Relative values of average logarthmic energy loss per collision, α, for collision of Br atom

system		
$He\text{-}CH_3Br\text{-}Br_2$	$\alpha_{\mathrm{He}}/\alpha_{\mathrm{CH_3Br}}$	0.27±0.03
$Xe\text{-}CH_3Br\text{-}Br_2$	$\alpha_{\mathrm{Xe}}/\alpha_{\mathrm{CH_3Br}}$	1.2±0.1
	$\alpha_{\mathrm{Xe}}/\alpha_{\mathrm{He}}$	4.5±0.5

Here X_i is the mole fraction of the ith molecule, and S_i is the collision cross-section for the Br-ith molecule collision. A plot of $-1/\ln(1-P)$ *versus* $(1-f)/f$ gave straight lines for the results in both He and Xe moderators as is shown in Fig. 3. The following values are obtained: (He) slope 4.8±0.5, intercept 18±2, (Xe) slope 22±2, and intrecept 18±2. The relative values of α obtained from the intercept/slope values in Fig. 3 have been summarized in Table 3. For the calculation of S, the diameters used for individual products[31] are: He, 2.2(Å); Xe, 4.9(Å); Br, 4.2(Å), Br_2, 8.4(Å), and CH_3Br, 5.4(Å). The above graphical analysis has been carried out on the basis of the sum of the yields of $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$. By contrast, the billiard-ball model predicts the ratio of 1.0 : 8.8 : 10.3 for $\alpha_{\mathrm{He}} : \alpha_{\mathrm{Xe}} : \alpha_{\mathrm{CH\ Br}}$. This suggests a high inelasticity in the actual collisions of recoil bromine, even with monatomic molecules.

Examination of the data in Figs. 1 and 2 shows that the ratio of the two products is almost constant at any mole fraction of the moderators within the range of experimental uncertainty.

---

27) R. Wolfgang, *Ann. Rev. Phys. Chem.*, **16**, 15 (1965).

28) C. M. Wai and F. S. Rowland, *J. Am. Chem. Soc.*, **90**, 3638 (1968).

29) P. J. Estrup and R. Wolfgang, *ibid.*, **82**, 2661, 2665 (1960).

30) R. Wolfgang, *J. Chem. Phys.*, **39**, 2983 (1963).

31) S. Chapman and T. J. Cowling, "The Mathematical Theory of Non-uniform Gases," Vniv. Press, Cambridge (1953), p. 229.

It is thus, likely that the chemical reaction range does not change significantly in the substitution reaction of H or Br in methyl bromide by the hot Br atom. This is accord with the similar dependencies of the yields upon the pressure.

The authors are grateful to Mr. T. Ohkubo for his assistance throughout this work. They also wish to express their gratitude to Dr. K. Motojima and the members of the Reactor Chemistry Laboratory in JAERI.